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54 Process for the preparation of N-phosphonomethyl glycine and N-phosphonomethyl glycine prepared thereby.

57 The invention provides a process and the product of process for the preparation of N-phosphonomethyl-glycine comprising the oxidation of an aqueous suspension of N-phosphonomethyl-imino diacetic acid in the presence of a catalyst with oxygen or an oxygen-containing gas.

Comparing the process of the invention with the known processes, specific conversion is considerably increased and significant amounts of energy can be saved.

PROCESS FOR THE PREPARATION OF N-PHOSPHONOMETHYL GLYCINE
AND N-PHOSPHONOMETHYL GLYCINE PREPARED THEREBY.

The present invention relates to an improvement
in the process for the preparation of N-phosphonomethyl
glycine by the oxidation of N-phosphonomethyl imino diacetic
acid with oxygen or an oxygen-containing gas in the
5 presence of a catalyst.

N-phosphonomethyl glycine has been known and
widely used for almost a decade for its herbicidal
activity. N-phosphonomethyl glycine (Glyphosate) is
suitable for the control of various monocotyledonous and
10 dicotyledonous annual and perennial undesired plants in case of
post-emergent treatment. A particular advantage of the
compound is that it does not possess any persistent
activity and thus it can be successfully employed in
crop rotations (Proc. N. Cent. Weed Control Conf. 26,
15 64 /1971/).

N-phosphonomethyl-glycine is most often prepared
by the oxidation of N-phosphonomethyl iminodiacetic acid.
One known process comprises oxidizing the starting
material with hydrogen peroxide (Dutch Terinzagelegging
20 No. 73 07 449). According to another
method the acetic acid group of the starting material
is split off by acid catalysed hydrolysis (Hungarian

Patent Specification No. 165 965).

Electrolytic oxidation is disclosed in German Federal Republic Patent Specification No. 2 363 634, US Patent Specification No. 3 859 183, and British Patent Specification No. 1 452 644. In the first of these references N-phosphonomethyl imino diacetic acid is subjected to anodic oxidation in acidic medium by using graphite electrodes, whereas the last two references relate to oxidation carried out on the tetraester group of N-phosphonomethyl imino diacetic acid and the desired end product is formed by hydrolysing the obtained N-phosphonomethyl glycine triester.

Oxidation of N-phosphonomethyl imino diacetic acid may also be carried out with oxygen or oxygen-containing gas in the presence of a catalyst (US Patent Specification No. 3 969 398, German Federal Republic Patent Specification No. 2 519 388 and Belgian Patent Specification No. 861 996). The advantage of the catalytical oxidation over the known methods mentioned above is that it does not require expensive chemicals or electrolysis equipment. Severe drawbacks of this method, however, come from the fact that N-phosphonomethyl-imino diacetic acid, used as starting material, is poorly soluble in water (saturation concentration of the compound at 25°C: 1 % by weight, at 95°C: 4 % by weight, and even at 150°C i.e. even in cases when operations are conducted at a higher pressure than normal pressure, the solubility amounts only to 10 % by weight (see German Federal Republic Patent Specification No. 2 519 388).

As a consequence of the minimal solubility of N-phosphonomethyl imino diacetic acid, aqueous solutions have to be employed in a large amount thereby reducing the useful capacity of the reactor and thus increasing the energy
5 required. A large amount of water has to be removed from the effluent requiring a further amount of energy. This process is thus uneconomical considering both utilization of capacity and energy balance.

In order to eliminate the disadvantages mentioned
10 above a method is disclosed in Belgian Patent Specification No. 861 996, according to which the salts of N-phosphonomethyl-imino diacetic acid are used as

starting material. Depending upon the character of the cation present, the salts of N-phosphonomethyl imino diacetic
15 acid form a 5-30% saturated solution with water at a temperature of 100 °C. From the point of view energy-saving, only those salts whose solubility is close to the upper limit of the saturated concentration may be used in large scale practice. Thus, for example, the isopropyl amine salt
20 of N-phosphonomethyl imino diacetic acid may be employed. Data disclosed in Belgian Patent Specification No. 861 996 show that during the oxidation of the compound a considerable amount of by-products is formed (such as N-methyl-N-phosphonomethyl glycine and methylamine methyl phosphonic acid),
25 which reduce the yield of the end-product and which may be removed from the end-product only with difficulty. Though the formation of by-products may be reduced if the conventionally-

used charcoal catalysts are replaced by a platinum catalyst (in which case the rate of the main reaction is selectively increased) side reactions however can never be eliminated completely. A further disadvantage is the low yield of the reaction: isopropylamine salt of N-phosphonomethyl glycine is obtained even in the most favourable case in the form of about 20 % aqueous solution, thus a large amount of water still has to be removed from the solution (about 50 %) if the product is formulated in the commercially available form of a 36 % aqueous solution. This process is however somewhat more economical than the previous process, but neither the purity of the product nor the energy balance of the process is satisfying.

According to the present invention the disadvantages of the above-mentioned currently known processes are largely eliminated by preparing pure N-phosphonomethyl glycine by an economic, energy-saving and capacity-increasing process.

We have now found that catalytic oxidation of N-phosphonomethyl imino diacetic acid may be carried out in suspension thus completely or almost completely converting N-phosphonomethyl imino diacetic acid to N-phosphonomethyl glycine with a great specific conversion (related to time units and identical liquid volumes).

The process according to the invention was not obvious in the light of the disclosure of German Federal Republic Patent Specification No.2519 388. On the contrary in the cited reference a process is disclosed

comprising the oxidation of N-phosphonomethyl imino
diacetic acid carried out in aqueous solutions and not
even the use of supersaturated solutions is suggested
because: "the precipitation of the starting material
5 can be expected whereby the reaction is slowing down and
the separation and purification of the product becomes
more difficult."

Similar conclusions could be drawn when con-
sidering the reaction mechanism of suspensions. As the
10 reaction may take place only on the boundary surfaces, it
could be expected that the reaction - if it takes place
at all - would be extremely slow from the beginning, the
rate of reaction would gradually decrease with accumulating
end-product and, on achieving a given concentration the
15 reaction would substantially come to an end, as the molecules
of the end-product formed on the boundary surface can
diffuse only very slowly into the inner part of the
liquid layer. Thus even in the most favourable cases only
very slow reactions could be expected in suspensions,
20 where 100 % conversion is not achieved. We have now
surprisingly found that the amount of the starting
material converted within one time unit (expressed in
grams) in a suspension is about twice that
amount obtained in the reaction conducted in liquid layer
25 and furthermore the starting material can be
completely converted to the end-product. It has to be
noted that none of the conventionally-used methods
to accelerate the reaction in suspensions

(such as pragrinding in a colloid mill, treatment with wetting agents etc.) need be used.

According to the present invention we therefore provide a process for the preparation of N-phosphonomethyl-glycine comprising the oxidation of an aqueous suspension of
5 N-phosphonomethyl-imino diacetic acid in the presence of a catalyst with oxygen or an oxygen-containing gas; the said suspension advantageously containing from 7 to 70 g, and preferably from 20 to 50 g, of N-phosphonomethyl-imino
10 diacetic acid per 100 ml of water.

According to a further aspect of the present invention we also provide N-phosphono-methyl-glycine whenever produced by the process of the present invention.

The content of N-phosphonomethyl-imino diacetic acid
15 of the aqueous suspension may vary within a relatively wide range. The lower limit is given by the solubility of N-phosphonomethyl imino diacetic acid at a given temperature, while the upper limit depends on the miscibility of the reaction mixture. If, for example, the reaction is carried
20 out at 100 °C, then 5% suspensions may be used as a lower limit, but obviously the use of suspensions containing 30-50% of solid is preferable.

Oxidation is carried out with oxygen or a gas mixture containing oxygen, such as air. If pure oxygen is employed
25 as the oxidant, the rate of reaction is higher than the rate of oxidation conducted with air, but considering the equipment, energy and labour requirements for the preparation of pure oxygen it is more economical to use air as the oxidant.

The reaction temperature may vary within relatively
30 wide limits. The reaction conveniently is carried out at a temperature ranging from temperature to 200 °C, preferably from

50 to 150 °C, more preferably from 70 to 120 °C.

The reaction may be conducted at normal pressure but the reaction rate is rather low when working under normal pressure. The reaction is preferably carried out at elevated pressure, such as, for example, 2-20 atm. It is particularly preferred if the reaction is conducted at 4-10 atm. Significant further improvement is not achieved at pressures in excess of the upper limit given above.

Oxidation is always conducted under shaking or stirring. The rate of shaking or stirring should be sufficient to give a homogeneous suspension, local inhomogeneities may slow down the reaction and thus the end products may contain impurities.

Those catalysts suitable for use in the process of the present invention include, for example, the known catalysts, such as powder formed or granular charcoal (e.g. German Federal Republic Patent Specification No. 2 519 388), noble metal catalysts on a carrier (e.g. platinum or palladium applied on activated charcoal), noble metal oxide catalysts (such as platinum oxide). Noble metal, preferably platinum or palladium, catalysts applied on activated charcoal ensure a higher initial rate of reaction than the activated charcoal catalysts, that is to say they act as rate increasing catalysts as disclosed in Belgian Patent Specification No. 861 996. Activated charcoal may be separated by simple filtration and it may be fully recovered by washing with hot water and by drying at 100-120 °C. The separated catalyst may be suspended in hot water during which oxygen or an

oxygen-containing gas, e.g. air, is introduced and the recovered catalyst subsequently is dried. The catalytic activity of the recovered catalyst does not significantly decrease even after 10 working cycles. On the other hand, according to Belgian Patent Specification No. 861 996, 5 activated charcoal when used as a catalyst for the oxidation carried out in a solution loses its activity after a few cycles and can no longer be removed.

According to the invention, however no significant 10 losses in the material were observed in the course of the recovery of the catalyst.

At least 5 mg. of catalyst are used per 1 g. of the starting material N-phosphonomethyl imino diacetic acid. The upper limit of the amount of the catalyst is for the 15 most part determined by economic factors. The amount of the catalyst may be for example 0.5-100%, preferably 5-60%, particular preferably 5-40% of the amount of N-phosphonomethyl imino diacetic acid.

N-phosphonomethyl glycine obtained according to 20 the process of the invention is shown by NMR spectroscopy to be in the form of a highly pure product. The obtained aqueous solution may be concentrated, if desired, according to the requirements of the user, or N-phosphonomethyl glycine may alternatively be separated in solid form. Solutions 25 obtained according to the invention and containing N-phosphonomethyl glycine may, after distilling off formaldehyde, be employed directly for agrochemical purposes.

Percentages herein refer to percentages by weight unless otherwise indicated.

The following Examples serve to illustrate the present invention without limiting the scope of protection sought therefor.

Example 1

5 The reaction is carried out in an acid-fast
200 ml. cylindrical steel tank equipped with a heating
jacket, thermometer, and an air-introducing and air-outlet
valve. To the reactor a solution of 4 g. of N-phosphono-
methyl iminodiacetic acid in 100 ml. of water at a
10 temperature of 100 °C is added and to the solution 0.4 g.
of Norit A catalyst is introduced. The reactor is
sealed, fixed on a shaker and air is introduced into the
reactor until a pressure of 6 atm is achieved. The
reaction is carried out at 90-95 °C under steady stirring
15 of the contents of the reactor. The formaldehyde and carbon dio-
xide formed during the reaction are blown out from the reactor
every 30 minutes. Under such conditions the reaction is
complete within 2.5 hours and 2.8 g. (100%) of
pure N-phosphonomethyl glycine are obtained (purity
20 verified by NMR spectroscopy). Specific conversion is
calculated according to the following formula:

$$\text{specific conversion} = \frac{\text{weight of end product (g.)}}{\text{volume of liquid (litre)} \times \text{reaction time (hour)}}$$

Specific conversion: 11.2 g./l.hour

Example 2

25 One may proceed according to Example 1 but as
starting material 100 g. of water, 20 g. of N-phosphono-
methyl imino diacetic acid and as catalyst 2 g. of Norit

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A are used. After a reaction time of 6.5 hours, 14 g. of N-phosphonomethyl glycine are obtained and thus the specific conversion amounts to 21.5 g./litres.hour. (1.9 times greater than that achieved according to Example 1).

Example 3

One may proceed as disclosed in Example 1 but as starting material 100 g. of water, 40 g. of N-phosphonomethyl imino diacetic acid and as catalyst 4 g. of Norit A catalyst are used. After a reaction time of 10 hours, 28.6 g. of pure N-phosphonomethyl glycine are obtained (verified by NMR spectroscopy). Specific conversion: 28.6 g./litres.hour (2.5 times greater than that obtained in Example 1).

Example 4

One may proceed as disclosed in Example 1 but as starting material 100 g. of water, 30 g. of N-phosphonomethyl imino diacetic acid and as catalyst 3 g. of Norit A catalyst are employed. After a reaction time of 8.5 hours, 21.2 g. of pure N-phosphonomethyl glycine are obtained (verified by NMR spectroscopy). Specific conversion: 24.9 g./litres.hour (2.2 times greater than that achieved according to Example 1).

Example 5

The reaction is carried out in a 2 litres acid-

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fast and pressure resisting steel autoclave equipped with a heating jacket, thermometer, air-introducing and air-outlet valve and paddle stirrer. To the autoclave 300 g. of N-phosphonomethyl imino diacetic acid, 1000 ml. of water and 30 g. of Norit A are introduced. The autoclave is sealed, the reaction mixture is heated to 90-95 °C, and air is led to the autoclave under the liquid level until 6 atm pressure is achieved. The suspension is stirred at a rate of 400 rpm. After a reaction time of 8.5 hours, 208 g. of pure N-phosphonomethyl glycine are obtained, the purity of which is checked by NMR spectroscopy. Achieved specific conversion: 24.4 g./litres.hour (2.2 times greater than that obtained by Example 1).

Example

When the reaction is completed, the catalyst is immediately filtered off, the mixture is washed with hot water and dried at 110 °C. The catalyst thereby recovered is used in further operations.

Example 6

One may proceed as disclosed in Example 5, but as starting material 1000 ml. of water, 200 g. of N-phosphonomethyl imino diacetic acid and as catalyst 20 g. of Norit A recovered as disclosed in Example 5 are used. After a reaction time of 6.5 hours, 146 g. of N-phosphonomethyl glycine, the purity of which is verified by NMR spectroscopy, are obtained. Achieved specific conversion: 22.4 g./litres.hour (twice the value obtained

in Example 1).

The catalyst is recovered as described in Example 5 and may be used in further operations.

Example 7

5 One may proceed as described in Example 1 but using as starting material 100 ml. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 2 g. of Norit A catalyst (the catalyst having been recovered after the reaction disclosed in Example 6). After a reaction time of
10 6.5 hours, 14.2 g. of pure N-phosphonomethyl-glycine are obtained, the purity of which is verified by NMR spectroscopy. Achieved specific conversion: 21.8 g./litres.hour (1.9 times greater than that achieved according to Example 1).

After recovery, the catalyst is used in five further
15 working cycles. The activity of the catalyst is not reduced.

Example 8

One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 5 %
20 palladium/charcoal (Carbo C Extra) are employed. After a reaction time of 5 hours, 14.4 g. of pure 4-phosphonomethyl glycine are obtained, the purity of which is verified by NMR spectroscopy. Achieved specific conversion: 28.8 g./litres.hour (2.5 times greater than that

obtained in Example 1).

Example 9

One may proceed as disclosed in Example 1 but as
starting material 100 ml. of water, 20 g. of N-phosphono-
5 methyl imino diacetic acid and as catalyst 2 g. of Carbo
C Extra are employed. After 7 hours reaction time,
14.3 g. of pure N-phosphonomethyl glycine are obtained
the purity of which was checked by NMR spectroscopy.
Achieved specific conversion: 20.8 g./litres.hours (1.85
10 times greater than the value achieved in Example 1).

Example 10

One may proceed as disclosed in Example 1 but as
starting material 100 ml. of water, 20 g. of N-phosphono-
15 methyl imino diacetic acid and as catalyst 2 g. of 5 %
platinum/charcoal (Carbo C Extra) are used. After a
reaction time of 4.5 hours, 14.2 g. of pure N-phosphono-
methyl glycine are obtained the purity of which is checked
by NMR spectroscopy. The achieved specific conversion:
20 31.5 g./litres.hours (2.8 times greater than the value
obtained in Example 1).

When comparing data of Examples 8 to 10, it can
be observed that by using noble metals the reaction
rate may be increased.

CLAIMS:

1. A process for the preparation of N-phosphonomethyl-glycine comprising the oxidation of an aqueous suspension of N-phosphonomethyl-imino diacetic acid in the presence of a catalyst with oxygen or an oxygen-containing gas.
2. A process as claimed in claim 1 wherein the aqueous suspension used as starting material contains from 7 to 70 g of N-phosphonomethyl-imino diacetic acid per 100 ml of water.
3. A process as claimed in claim 1 wherein the aqueous suspension used as starting material contains from 20 to 50 g of N-phosphonomethyl-imino diacetic acid per 100 ml of water.
4. A process as claimed in any one of claims 1 to 3 wherein the oxygen-containing gas used to effect the oxidation is air.
5. A process as claimed in any one of claims 1 to 4 wherein the said oxidation is effected at an elevated pressure.
6. A process as claimed in any one of claims 1 to 5 wherein the said catalyst comprises activated charcoal.
7. A process as claimed in claim 6 further comprising the separation by filtration of the activated charcoal catalyst after the oxidation, and the recovery of the separated catalyst by washing with hot water and drying at 100 to 120°C.
8. A process as claimed in claim 7 wherein the washing of the catalyst is effected with hot water during the introduction of oxygen, air or another oxygen-containing gas.

9. N-phosphonomethyl-glycine whenever prepared by a process as claimed in any one of claims 1 to 8.